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PRINCIPLES OF ESCA AND APPLICATION TO METAL CORROSION. COATING AND LUBRICATION

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METAL CORROSION, COATING AND LUBRICATION

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ABSTRACT

The principles of ESCA (electron spectroscopy for chemical analysis) are described by comparison with other spectroscopic techniques. The advantages and disadvantages of ESCA as compared to other surface sensitive analytical techniques are evaluated. The use of ESCA is illustrated by actual applications to oxidation of steel and Rene' 41, the chemistry of lubricant additives on steel, and the composition of sputter deposited hard coatings. Finally, a bibliography of material that is useful for further study of ESCA is presented and commented upon.

I. INTRODUCTION

ESCA (electron spectroscopy for chemical analysis)¹ is also known as x-ray photoelectron spectroscopy or XPS. Like optical spectroscopy, it consists of analyzing the radiation from atoms which have been excited. The nature of the radiation is different, the analyzer is different and the excitation source is different from optical spectroscopy. However, all spectrographic techniques share the basic idea that the character of the radiation identifies the radiating atom and the amount of the characteristic radiation is related to the amount of that type of atom in the excited specimen. A schematic comparison between ESCA and optical spectroscopy is drawn in figure 1.

In ESCA, x-rays with a single energy cause electrons to be ejected from atoms of the sample, and the analyzer detects these electrons. The energies of the electrons are characteristic of the atoms from which they came and of the oxidation state of those atoms. The number of electrons ejected depends on the number of sample atoms exposed to the x-rays. Thus, the technique provides semiquantitative elemental analysis along with some chemical information.

The material of this paper will be presented in three sections. The first, titled, ESCA Fundamentals will describe the technique, the second, entitled Comparison to Other Analysis Techniques will make comparisons to other surface analytical methods and the third, with

the heading Applications will discuss uses. A brief bibliography will follow these sections for those interested in greater detail.

II. ESCA FUNDAMENTALS

Each element of the process shown schematically in figure 1 contributes some of the characteristics peculiar to ESCA. Monochromatic x-rays are used. Thus when all of an x-ray photons energy is given to an electron, the electron will be ejected from the atom with a kinetic energy equal to the photon energy minus the binding energy of the electron in the atom:

$$E_{kin} = E_{x-ray} - E_B$$

It is because of the unique electron binding energies for each atom that the electron kinetic energies are characteristic of the atom. Any uncertainty in E_{x-ray} will cause a spread in E_{kin} which will show up as a broad spectral peak. Low energy characteristic x-rays are most nearly monochromatic. For this reason the usual x-rays used are AlK_{α} or MgK_{α} .¹

If charge is transferred to or from an atom, as it is when the atom shares in a chemical bond, the binding energy of all the electrons shifts. This causes a change in E_{kin} - "The Chemical Shift" - which can be detected. X-rays cannot, of course, be focused. Therefore in most instruments the entire sample is flooded with x-rays, and the spatial resolution of the instrument is determined by the sample area which is "seen" by the analyzer. This depends on the kind of analyzer used, but is always much larger than the area excited by focused electron or ion beams in typical microanalytic spectroscopies.

Because the x-ray energies are low, the energies of the ejected electrons are all less than about 1 keV. In a solid sample such electrons cannot travel more than about 20 Å without losing energy. Thus the characteristic lines in the spectrum are due mainly to electrons from atoms in the top 10 atomic layers of the sample.²

The intensity or number per second of electrons from a particular kind of atom which reach the analyzer is proportional to the number of that kind of atom in the sample. This intensity is diminished by absorption and scattering of the electrons before they leave the sample. Thus, the same concentration of an atom in a highly absorbing matrix would give lower intensity than in a less dense matrix. This "matrix effect" is common to all spectroscopies. Consequently, ESCA is semi-quantitative.

In order that the electrons travel undisturbed from sample to analyzer they must travel in a vacuum. Further since the analysis is surface sensitive, it is imperative that this be ultra-high vacuum. Thus, the specimen must be compatible with pressures of 10^{-8} Torr.

Low energy x-rays are usually not destructive to the sample, although in some cases they can cause disruption of organic molecules. If it is permissible to etch the samples, an ion gun can be incorporated in the sample chamber. Sputtering is the removal of atoms from a surface when they are struck by energetic ions - in this case inert gas ions with energies from several hundred to several thousand eV. The ion gun can be used to sputter clean the sample surface and also to obtain information on sample composition vs. depth - a "depth profile." The method is to analyze the sample surface, sputter away the surface layer with the ion gun, then analyze again and repeat the entire process until the layer of interest is completely removed. These energetic ions can cause reduction of surface oxides and this must be kept in mind when they are used.

The analyzer contributes to the sensitivity of the technique as well as the spatial resolution, and the energy resolution or ability to detect chemical differences. There are many varieties of analyzers. In general one expects sensitivity of 0.1 atomic percent in the bulk or about 1 percent of a single atomic layer on a surface. Energy resolution of the technique is limited more by the energy spread of the x-rays than the analyzer. Shifts of about >0.1 eV can be detected. The analyzed area ranges from 2 mm diameter to several cm^2 depending on the type of analyzer.

Finally, ESCA is sensitive to all elements heavier than hydrogen, although the sensitivity varies with the element and with the particular atomic level being detected.^{2,3}

Because the term $E_{\text{x-ray}}$ in the basic equation $E_{\text{kin}} = E_{\text{x-ray}} - E_{\text{B}}$ is usually precisely known from diffraction experiments, the spectrum can be plotted as a function of E_{kin} or E_{B} . The latter is the more common with the scale going right to left as indicated in figure 1. Actually the equation is not quite correct as it stands. A term for the work function of the analyzer should be included. This is often not known a priori.

It is customary to use one binding energy as a standard to calibrate the instrument and to relate all others to it. In earlier work the C(1s) line was used because it was always present due to diffusion pump oil backstreaming. In modern systems this is very unsatisfactory. The Au(4f_{7/2}) binding energy of 84.0 eV is now commonly used, and many systems use an evaporator to deposit a partial monolayer of gold on the surface of a sample for calibration purposes.

III. COMPARISON TO OTHER ANALYSIS TECHNIQUES

Most analytical techniques sample the bulk properties of the material. X-ray fluorescence, for example probes several thousand Angstroms below the surface. Surface sensitivity is important when layers too thin to detect with XRF must be analyzed. A depth profile is important if the thickness of coatings thinner than $1\text{ }\mu\text{m}$ must be measured or if the layer to be analyzed is beneath a thin coating. The techniques discussed here are also useful when light elements must be analyzed.

The techniques that are surface sensitive and provide elemental analysis are, in addition to ESCA, Auger Electron Spectroscopy, AES, Ion Scattering Spectrometry, ISS, and Secondary Ion Mass Spectrometry, SIMS. In both ISS and SIMS the sample surface is bombarded with inert gas ions. ISS measures the energy of the ions that rebound from collisions with surface layer atoms. This energy is related to the mass of the surface atom. SIMS uses a mass spectrometer to detect atoms and molecular fragments sputtered from the surface layer. In AES atoms are excited by an electron beam and the electrons emitted by excited atoms are analyzed.

Figure 3 is a comparison of some of the important characteristics of the four techniques. ESCA has two major deficiencies compared to the other techniques. First, it is the only one that is incapable of microanalysis or imaging, although many commercial SIMS instruments also share this difficulty. Secondly, it is the slowest method. That is not a serious drawback when analyzing for one or two elements at reasonably large concentrations, because sample changing time may be the most time consuming part of the process in any ultra-high vacuum apparatus. However, for complete analyses, trace element analysis, or depth profiling the time factor is serious. Commercial instruments that combine ESCA and another method such as Auger are then desirable.

On the positive side, only Auger, ESCA, and ISS give semiquantitative results. In the case of Auger this is only possible if there are no changes in spectral line shape, and ISS has very limited resolution for high mass numbers. Furthermore, of the four techniques only ESCA combines quantitative and chemical information.

When ion sputtering is used, the specimen surface is often altered chemically and quantitatively. Only SIMS gives a spectrum characteristic of the unaltered surface. However, it is a difficult spectrum to interpret because of severe matrix effects. Recent results with ISS indicate that in some systems a certain amount of surface structural information is available. This is in studies of monolayer adsorption on perfect crystal surfaces and may not be useful for routine analysis. The extremely shallow depth resolution of SIMS and ISS is also unlikely to be an advantage in routine analysis.

IV. APPLICATIONS

Some applications of ESCA have been selected from work performed at NASA. They are chosen to illustrate the various characteristics of ESCA discussed previously. Attention will be focused on the importance of these characteristics to the conclusions drawn, rather than on the significance of the experiment itself. In some cases only part of the results of a study are included since that sufficiently illustrates the use of ESCA.

A. Analysis of Fe-Cr Alloys

To illustrate the quantitative aspects of ESCA two iron-chromium alloys Fe-14% Cr and 440-C (16-18% Cr) were analyzed. The samples were metallurgically polished then sputtered until no oxygen could be detected in the ESCA spectrum. The areas of the iron and chromium 3p peaks were measured. The relative sensitivities for these peaks are available in the literature.^{2,3} Figure 4 shows typical Fe(3p) and Cr(3p) peaks with the background level drawn in. The enclosed areas were measured. The figure shows the results for the two alloys. Both analyze somewhat rich in chromium. This could also be due to inaccuracy of the published sensitivities. It is possible, too, that sputtering changed the composition of the analyzed surfaces.

The relative sensitivities can also be found by analyzing standards. In this case pure Cr and pure Fe were used. This is not the best choice but the results were 13% for the 14% alloy and 18% for the 440-C. There is some danger in addition to the usual matrix effects in the use of standards. Because the analysis is surface sensitive, differences in surface preparation, contamination and even geometrical orientation of the samples can change the observed intensities. Thus, the results from published sensitivities might be preferred in this case, because these factors were eliminated in their measurement. In any event, the limit of accuracy is a few percent in concentration.

B. Oxidation of Rene' 41

To illustrate the chemical information available from ESCA, the oxidation of a Ni-Cr alloy (Rene' 41) is considered. Two specimens were prepared by metallurgical polishing. They were oxidized at 550 °C in air for 24 hours and 120 hours respectively. Figure 5 shows the Ni(2p $3/2$) peak from the 24 hour sample after sputter etching it for 1/2, 5 and 160 minutes. The lines in the figure show the positions of the peaks that would be produced by oxidized and unoxidized Ni. Since longer sputter etching time causes removal of even deeper material,

the change from an oxidized surface to a metal substrate is clear. The same analysis can be done for Cr.

If the heights of each peak are plotted against sputter etching time, the result is a depth profile like that of figure 6. Here the outer surface is on the left and the metal bulk is to the right at long sputter etching times. The surface is apparently a mixture of oxides with an underlying Cr_2O_3 layer. The Ni metal in the surface is probably due to nickel oxide which is reduced by sputtering. A separate study of pure NiO would clarify this point.

Figure 7 shows the equivalent depth profile for the 120 hour specimen. In this time the outer NiO layer has grown thicker, but there is still an underlying Cr_2O_3 layer. The change in the nature of the oxide surface with increasing oxidation time was of interest in studies of coating adhesion.

C. Adhesion of Sputtered Coatings⁴

In this example all the properties of ESCA are used in an attempt to understand the effect of intermediate layers on the adhesion of some sputtered refractory compounds onto steel. The refractory compounds Mo_2C , and Mo_2B_5 were deposited by RF sputtering on 440-C steel substrates. Each coating was deposited twice: once on a heavily oxidized substrate, and once on a clean substrate. It was found that the adhesion of both Mo_2C and Mo_2B_5 to clean substrates was poor.⁵ The adhesion of Mo_2B_5 to oxidized 440-C was also poor but the adhesion of Mo_2C was markedly better on the oxidized substrate.

Depth profiles of both films on both types of substrates were made in hopes of discovering the cause for the different effects which the substrate oxidation had on the two coatings.

The profiles of most significance are shown in figures 8 and 9. In these profiles the horizontal axis has been marked in Angstroms depth in the film by measuring the sputtering rate on some films of known thickness. The vertical axis was calibrated in mole percent of each film constituent by internal determination of instrument sensitivity. This was done by using the known compositions of substrate and film to get the sensitivities for their constituents. The sensitivity to the oxides in the interfacial region was determined by requiring that all constituents add to 100 percent. A more refined version of this technique has been described recently in the literature.^{6,7}

The difference between the two interfacial regions seems to be mainly the extent to which the oxides of the film material which form during the initial stages of sputtering⁸ are mixed with the iron

oxide of the substrate. The MoO_2 and Fe_3O_4 are mixed throughout the interfacial region in the case of Mo_2C . However in the case of Mo_2B_5 there is a degree of segregation of the oxides. The improved adhesion of Mo_2C on oxidized 440-C may be due to the mixing of the oxides. Perhaps a graded spinel structure is formed in the interface.

D. Lubricant Additive Chemistry^{9,10}

A common oil additive is dibenzyl-disulfide (DBDS) which is intended to prevent severe wear or scuffing of parts under lubricant starved conditions. ESCA was used to determine whether DBDS reacted with the metal surface and if so, under what conditions, and in what way. Steel samples were rubbed together in a rather conventional wear test in such a way that the worn area was several millimeters in size. Both mild and severe wear could be produced by changing the load between the rubbing surfaces.

Figure 10 presents some of the results of ESCA analysis of the wear scars. The first point to notice is the importance of sputter cleaning the surfaces to remove contamination from exposure of the sample to air. The sulfate and part of the oxygen appear to be such contamination. The spectra also show that the reaction product on the surface is probably iron sulfide. Possible organic materials such as DBDS itself or benzyl mercaptide all have sulfur (2p) binding energies near 163.0 eV. Finally, it is clear that when the wear is severe there is a decrease in the metal oxide and a corresponding increase in the sulfide. One interpretation of this is that when the wear is severe the oxide layer is disrupted. The underlying metal is then exposed to the oil and reacts with the DBDS to form a sulfide.

The oxygen (1s) peak could be resolved as shown in figure 11 by using an analog curve resolver. This allowed a calculation of the chromium oxide to iron oxide ratio which was found to be about 20 percent in all cases. This is the same as the bulk concentration of the elements in the 304 stainless steel used. In this case the relative sensitivity is not considered because it is the same for all components of the same peak. Matrix effects also are the same.

V. BIBLIOGRAPHY

A. Books

ESCA, Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy; Kai Siegbahn, et al; Almquist and Wicksells, Uppsala (1967)

This is a classic work which explains the physics of ESCA and describes its development and early applications in Professor Siegbahn's

laboratory. Since the instruments described are not commercially available and much of the data has been improved since it is useful primarily for its lucid explanation of the basic principles.

Handbook of Spectroscopy, vol. I; J. W. Robinson, ed. CRC Press, Cleveland (1974)

Along with many other tabulations, this book contains a table of binding energies taken from the literature. The chemical state of the sample is identified and the method of calibrating the binding energy is indicated. Since much early work was done in poor vacuum systems which caused surface contamination problems and since the method of calibrating the binding energy is crucial, the user of this table must be wary. It is useful as a guide to the original papers, however in many cases more reliable values have been published since this table.

B. Review Articles

Review articles appear occasionally. A few useful ones are listed here without an attempt to be comprehensive.

David M. Hercules, "Electron Spectroscopy" Analytical Chemistry, vol. 42, no. 1 (1970) pg. 20A

David M. Hercules, "Electron Spectroscopy II. X-ray Photoexcitation" Analytical Chemistry vol. 44, no. 5 (1972) pg. 106R

Dean E. Eastman and Marshall I. Nathan, "Photoelectron Spectroscopy" Physics Today, April 1975, pg. 44

Robert S. Swingle, II and William M. Riggs, "ESCA" CRC Critical Reviews in Analytical Chemistry, October 1975, pg. 267

The last is the most thorough discussion while the first two give a literature review up to their dates of publication. The Physics Today article is one of a series of articles on surface physics in that issue.

C. Periodicals

Techniques of ESCA and fundamental surface studies are published in Surface Science and Journal of Electron Spectroscopy and Related Phenomena. Applications of general interest often appear in Analytical Chemistry, Journal of Chemical Physics and Journal of Vacuum Science and Technology. The first two of these are often the source of definitive values for binding energies in particular compounds. Applications of special interest will be published in whichever journal is appropriate. Corrosion Science, Journal of Applied Physics, Transactions of the Faraday Society, and many others could be of interest. Since the technique is becoming widely used the literature relating to applications is rapidly expanding.

VI. CONCLUSION

This review has not dealt with the details of the use of ESCA. Space would not permit that. Instead an attempt has been made to characterize the technique and point out its major advantages and limitations. These were contrasted with some similar techniques for perspective and also because a choice must often be made between these techniques. Some applications were discussed in order to make the important characteristics of ESCA more concrete. Finally, it is hoped that the bibliography will serve as a guide to deeper study of ESCA.

VII. REFERENCES

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3. "Hartree-Slater Subshell Photoionization Cross-Sections at 1254 and 1487 eV," by J. H. Scofield, J. Elec. Spec. Rel. Phenom., Vol. 8, p. 129, 1976.
4. Wheeler, Donald R. and Brainard, William A. E-9374, NASA TP-1161.
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6. "Quantitative Approach of Auger Electron Spectrometry, I - A Formalism for the Calculation of Surface Concentrations," by F. Pons, J. LeHericy, and J. P. Langeron, Surface Sci., Vol. 69, p. 565, 1977.
7. "Quantitative Approach of Auger Electron Spectrometry, II - Experimental Part," by F. Pons, J. LeHericy, and J. P. Langeron, Surface Sci., Vol. 69, p. 547, 1977.
8. "X-ray Photoelectron Spectroscopy Study of Radiofrequency Sputtered Chromium Bromide, Molybdenum Disilicide, and Molybdenum Disulfide Coatings and Their Friction Properties," by D. R. Wheeler, and W. A. Brainard. NASA TN D-8482, 1977.
9. "X-ray Photoelectron Spectroscopic Study & Surface Chemistry of Dibenzyl-Disulfide on Steel Under Mild and Severe Wear Conditions," by D. R. Wheeler. NASA TN D-8460, 1977.
10. Wheeler, Donald R. Wear 47, 243, 1978.

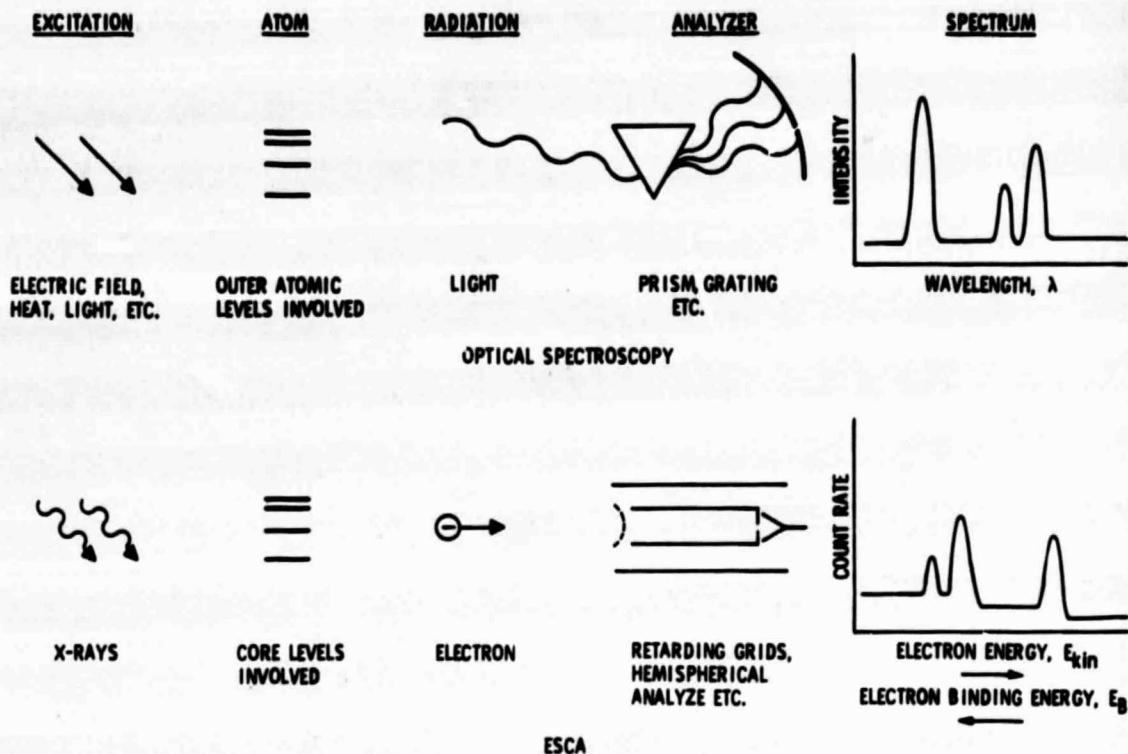


Figure 1. - Comparison of optical spectroscopy with ESCA.

$$E_{kin} = E_{x-ray} - E_B$$

$$E_{x-ray} = \begin{cases} 1253.6 \text{ eV} & \text{MgK}\alpha \\ 1486.7 \text{ eV} & \text{AlK}\alpha \end{cases}$$

CHEMICAL SHIFT IN E_B DURING BONDING

SPATIAL RESOLUTION $> 2 \text{ mm}$

SURFACE SENSITIVE

SEMIQUANTITATIVE

SAMPLE ENVIRONMENT $< 10^{-8} \text{ torr}$

NONDESTRUCTIVE

DEPTH PROFILES POSSIBLE

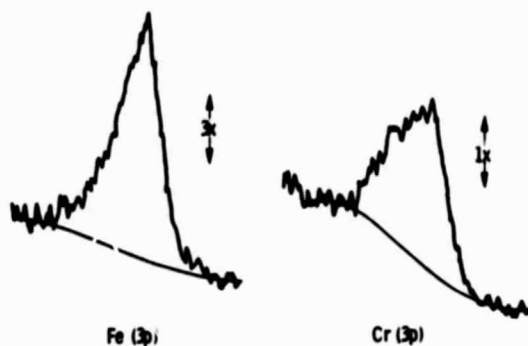
SENSITIVITY $\begin{cases} \sim 0.1 \text{ at } \% \\ \sim 1\% \text{ OF A MONOLAYER} \end{cases}$

ALL ELEMENTS EXCEPT H

Figure 2 - Features of ESCA.

	AUGER	ESCA	ISS	SIMS
SPATIAL RESOLUTION, IMAGING	3 μ m ELEMENTAL MAPS	>2 mm NO SCANNING	100 μ m SCANNING	LARGE AREA TO 100 μ m ION MICROPROBE ~5 μ m
DEPTH RESOLUTION, PROFILING	~20 Å CONTINUOUS PROFILES	~20 Å STEP PROFILES	1 ATOM LAYER CONTINUOUS PROFILES	1 ATOM LAYER CONTINUOUS PROFILE NECESSARILY
CHEMICAL INFORMATION	POSSIBLY NOT WELL UNDERSTOOD YET	YES	NO LOSSES ELEMENTAL DISCRIMINATION AT HIGH MASS NUMBER	YES BUT INTERPRETATION IS UNCLEAR
QUANTITATIVE	SEMI-QUANTITATIVE IN SOME SYSTEMS	SEMI	SEMI	DIFFICULT AND UNRELIABLE
SENSITIVITY	0.1% BULK 0.01 MONOLAYER	0.1% BULK <0.1 MONOLAYER	<0.01 MONOLAYER	ppm
SAMPLE CONSIDERATION	INTENSE ELECTRON BEAM, MODIFIES CHEMISTRY OF SURFACE	X-RAY BEAM HAS LITTLE EFFECT ON SAMPLE	LESS DAMAGE THAN AUGER. SPUTTER RATE CAN BE VERY LOW	ANALYSIS NOT MUCH ALTERED BY DAMAGE POLYMERS AND BIOLOGICAL SPECIMENS POSSIBLE
SPEED AND SIMPLICITY	FASTEST ELEMENTAL DATA EASY QUANTITATIVE AND CHEMICAL DATA HARDER	SLOWEST DATA EASILY INTERPRETED	CAN BE AS FAST AS AUGER. EASY TO INTER- PRET FOR LIGHT ELEMENTS	INTERMEDIATE SPEED RELATIVELY MOST DIFFICULT TO INTERPRET

Figure 3. - Comparison of features of surface analytic techniques.



ALLOY	PEAK	AREA UNDER PEAK	RELATIVE SENSITIVITY	wt % Cr
Fe-14% Cr	Cr3p	22	1.03	15.7
	Fe3p	145	1.39	
440-C 16 - 18% Cr	Cr3p	35	1.03	21
	Fe3p	155	1.39	

Figure 4. - Example of ESCA analysis of Fe-Cr alloys.

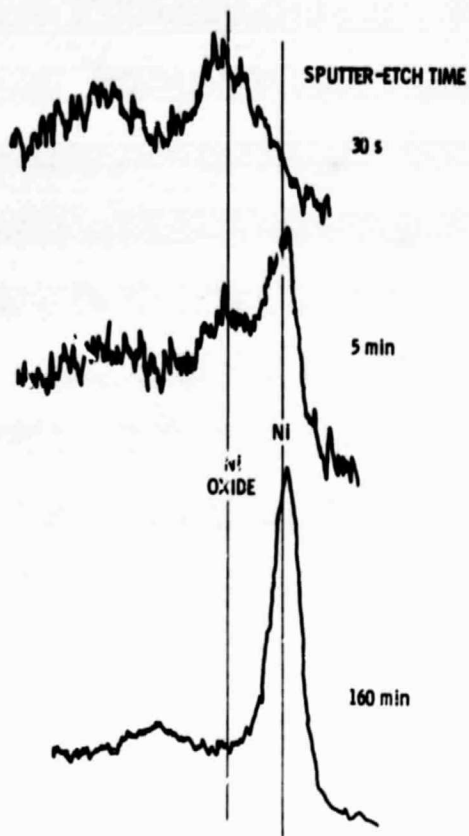


Figure 5. - $\text{Ni}(2p_{3/2})$ peak from Rene'41 oxidized 24 hours at 550°C , after sputter etching for 1/2, 5, and 160 minutes.

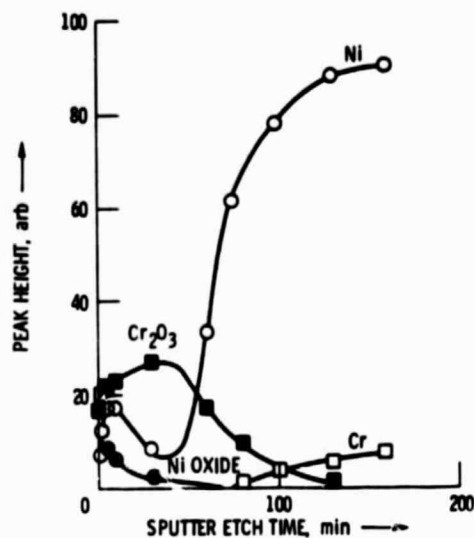


Figure 6. - Depth profile of Rene'41 oxidized 24 hours at 550°C .

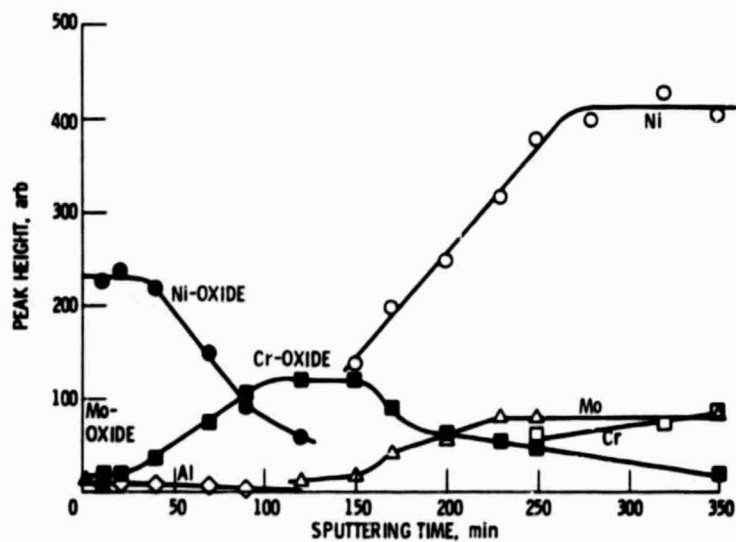


Figure 7. - Depth profile of Rene 41 oxidized 20 hours at 550°C .

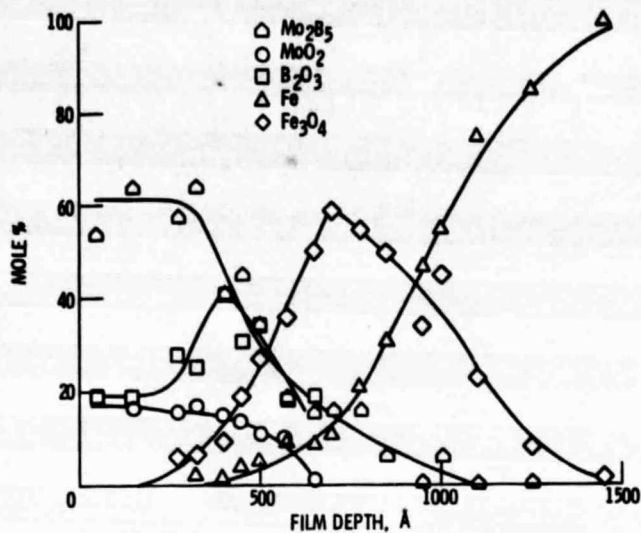


Figure 8. - Depth profile of Mo_2B_5 radiofrequency sputtered onto oxidized 440C substrate. Bias, -300 volts.

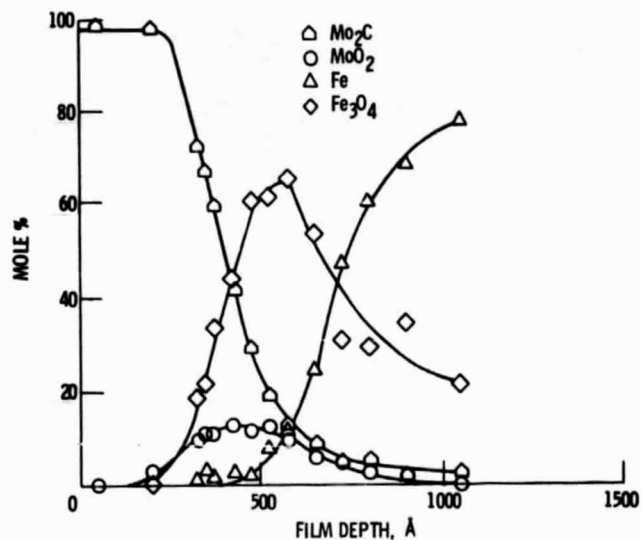


Figure 9. - Depth profile of Mo_2C radiofrequency sputtered onto oxidized 440C substrate. Bias, -300 volts.